

DATA EVALUATION RECORD

STUDY 6

CHEM 112600	Prohexadione calcium	§163-1
CAS No. 127277-53-6		
FORMULATION--00--ACTIVE INGREDIENT		

STUDY ID 44457787

Goetz, A. J., and C. Mills. 1996. Adsorption/desorption of ¹⁴C-BAS 125 W on soil. BASF Reg. Document No.: 96/5095. Unpublished study performed by BASF Corporation, Research Triangle Park, NC, and AGVISE Laboratories, Inc., Northwood, ND; and submitted by BASF Corporation, Research Triangle Park, NC.

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CONCLUSIONS

Mobility - Leaching & Adsorption/Desorption

1. This study is scientifically valid and satisfies the Subdivision N data requirement for the soil adsorption/desorption of prohexadione calcium (BAS 125 W).
2. The mobility of cyclohexene ring-labeled [3,5- ^{14}C]prohexadione calcium (BAS 125 W), at nominal concentrations of 0.14, 0.60, 1.1, and 2.2 ppm (0.14, 0.64, 1.3, and 2.2 ppm for loamy sand soil), was determined in sand, clay, chloroform fumigated loamy sand, and loam soil:solution slurries that were equilibrated for 24 hours at $25 \pm 2.0^\circ\text{C}$ in darkness. Freundlich K_{ads} values were 0.45 for the sand soil (0.5% OM), 2.8 for the clay soil (3.1% OM), 9.2 for the loamy sand soil (1.1% OM), and 11.1 for the loam soil (4.5% OM); corresponding linearized K_{dl} were 0.50, 2.8, 9.1, and 11.0; and corresponding K_{oc} values were 173, 155, 1428, and 421 mL/g. Freundlich K_{des} values were 11.2 for the sand soil, 0.71 for the clay soil, 0.23 for the loamy sand soil, and 0.31 for the loam soil. Respective $1/N$ values were 1.3, 1.0, 0.83, and 0.96.
3. Prohexadione calcium mobility appears to be dependent on the soil type. According to the McCall classification (McCall *et al.*, 1980) prohexadione calcium showed very high mobility potential in the sand soil ($K_{\text{dl}} = 0.50$; $K_{\text{oc}} = 173$) and low mobility potential in the loamy sand soil ($K_{\text{dl}} = 9.1$; $K_{\text{oc}} = 1428$).

METHODOLOGY

Based on the results of a preliminary study of the adsorption of cyclohexene ring-labeled [3,5- ^{14}C]prohexadione calcium (BAS 125 W, calcium 3-oxido-4-propionyl-5-oxo-3-cyclohexenecarboxylate; radiochemical purity 99.1%, specific activity 18.3 mCi/mmol; p. 9) to sand (Fuquay-Varine, NC, 96% sand, 2% silt, 2% clay, 0.5% OM, and pH 6.9), loam (Savoy, IL, 29% sand, 48% silt, 23% clay, 4.5% OM, and pH 6.3), clay (Red River Valley, ND, 17% sand, 29% silt, 54% clay, 3.1% OM, and pH 6.5), and chloroform-fumigated loamy sand (Fuquay-Varine, NC, 80% sand, 14% silt, 6% clay, 1.1% OM, and pH 5.7) soils, an adsorption equilibration period of 24 hours was chosen (pp. 13-15; Figure 1, p. 38). The loamy sand soil was sterilized via fumigation with chloroform vapors to decrease the microbial degradation of [^{14}C] BAS 125 W to $^{14}\text{CO}_2$ (see Comment #1). In a preliminary study, adsorption of the test compound to the glass culture tubes was not observed (p. 14; Figure 1, p. 38). In a preliminary stability study, the parent compound was determined to be stable in clay soil:0.01 M CaCl_2 solution slurries that were equilibrated for 24 hours (p. 20); the parent accounted for 94.1-94.3% of the applied radioactivity following 24 hours (Table 3, p. 30).

For the adsorption phase of the definitive study, aliquots (10 mL) of 0.01 M CaCl_2 solution treated with cyclohexene ring-labeled [3,5- ^{14}C]prohexadione calcium (dissolved in 0.1 N HCl, acetonitrile, and acetone, 2.5:7:15, v:v:v; p. 10), at nominal concentrations of 0.14, 0.60, 1.1, and 2.2 ppm (0.14, 0.64, 1.2, and 2.2 ppm for loamy sand soil), were added to glass culture tubes containing subsamples (2 g) of air-dried, sieved (2 mm) sand, loam, clay and loamy sand soils (Table 2, p. 29). Duplicate samples were prepared for each soil type/treatment rate combination. The soil:solution slurries (1:5, w:v) were equilibrated by shaking for 24 hours at $25 \pm 2.0^\circ\text{C}$ in darkness (p. 17). Following the adsorption equilibration period, samples were centrifuged and the supernatants decanted. Each supernatant was analyzed for total radioactivity by LSC. LSC detection limits were not reported.

To determine stability, adsorption supernatants from samples treated at the highest concentration (2.2 ppm) were analyzed by HPLC (Hamilton PRP-1 and YMC ODS-AQ columns) using a mobile phase gradient of (A) water:trifluoroacetic acid (1000:1, v:v) and (B) acetonitrile:TFA (1000:1, v:v; A:B, 95:5 to 90:10 to 60:40 to 40:60 to 5:95, v:v) with radioactive flow detection (p. 11-13). Eluent fractions were collected at one-minute intervals and analyzed by LSC. Based on HPLC analysis, the parent compound was stable in the supernatants of the sand, clay, loam, and the corresponding average recoveries of the parent compound were 95.8%, 94.4%, 91.4%, and 86.4% of the initial radioactivity (Table 6, p. 33). The stability of parent across all fortification levels used in the adsorption study was not investigated.

Twenty four hour stability test of BAS 125 W in 0.01 M CaCl_2 with clay soil was conducted. 65 μg of BAS 125 W was added to tubes containing 2 g of soil and 10 ml of 0.01 M CaCl_2 solution. The tubes were capped, vortexed to mix, and placed in the shaker in the dark at 25°C . After 24 hours the supernatant and the soil were separated and BAS 125 W was analyzed via HPLC. The average purity of BAS 125 W in the supernatant was $94.2 \pm 0.2\%$ (Table 3).

For the desorption phase of the definitive study, an aliquot of pesticide-free 0.01 M CaCl_2 solution equal to the volume of supernatant that was decanted following the adsorption phase was added to the soil pellets from the adsorption phase of the study (p. 17). The samples were equilibrated by shaking for 24 hours at $25 \pm 2.0^\circ\text{C}$. Following equilibration, the soil:solution slurries were centrifuged and the supernatants decanted. Each supernatant was analyzed for total radioactivity by LSC.

Following desorption, triplicate subsamples of dried (105°C) soil were analyzed by LSC following combustion (p. 17); combustion efficiency was determined with [^{14}C] reference standards (pp. 11, 12). It was not reported whether data were corrected for the combustion efficiency.

THE STUDY AUTHOR'S DATA SUMMARY

Freundlich K_{ads} values were 0.45 for the sand soil (0.5% OM), 2.8 for the clay soil, 9.2 for the

loamy sand soil, and 11.1 for the loam soil (4.5% OM.; Table 8, p. 35); corresponding K_{oc} values were 157, 157, 1445, and 424 mL/g. Respective $1/N$ values were 1.2, 0.98, 0.98, 0.99 for adsorption (Table 5, p. 32). Freundlich K_{des} values determined following a 24-hour equilibration period were 11.2 for the sand soil, 0.71 for the clay soil, 0.23 for the loamy sand soil, and 0.31 for the loam soil; respective $1/N$ values were 1.3, 1.0, 0.83, and 0.96 for desorption (Table 7, p. 34).

During the 24-hour equilibration period, $69.9 \pm 0.8\%$ of the applied radioactivity was adsorbed to the loam soil (across all application levels), $66.2 \pm 2.3\%$ of the applied was adsorbed to the loamy sand soil, $37.4 \pm 1.0\%$ of the applied was adsorbed to the clay soil, and $6.4 \pm 1.8\%$ of the applied was adsorbed to the sand soil (Table 4, p. 31). Following a 24-hour desorption equilibration period, $71 \pm 10\%$ of the adsorbed radioactivity was desorbed from the sand soil (across all application levels), $39 \pm 3\%$ of the adsorbed radioactivity was desorbed from the clay soil, $22 \pm 4\%$ of the adsorbed radioactivity was desorbed from the loamy sand soil, and $25 \pm 2\%$ of the adsorbed radioactivity was desorbed from the loam soil (Table 8, p. 35).

Across all application levels material balances were 94.8-100.3% for the sand soil, 90.3-93.3% for the clay soil, 94.3-99.3% for the loamy sand soil, and 89.3-93.6% for the loam soil (Appendix 4, pp. 70-73).

THE REVIEWERS' COMMENTS

1. According to the McCall classification (McCall *et al.*, 1980) in different soil types prohexadione calcium showed from very high (the sand soil) to low mobility (the loamy sand soil) potential.
2. The Freundlich adsorption coefficient may not be an adequate representation of adsorption across all concentrations and it cannot be assumed that K_f is equal to K_d . One of the $1/N$ values (1.2) for adsorption was not within the range of 0.9 to 1.1 (Table 5, p. 32). Others were 0.98 or 0.99. There was no linear relationship between the soil organic carbon content and the K_d for different soil ($r^2 = 0.28$). It is also noted that only 6.4% of the applied radioactivity was adsorbed to the sand soil during the adsorption equilibration period. An adsorption of 20-80% is necessary for the valid use of the Freundlich equation. Freundlich K_f values, corresponding linearized K_{dl} - determined via linearization method (van Genuchten *et al.*, 1977), and corresponding K_{oc} values are shown in the table below.

Soil	%OM	$1/n$	K_f	Adj. Factor ¹	K_{dl} ²	K_{oc} ³
sand	0.5	1.16	0.455	1.104	0.502	173
clay	3.1	0.98	2.826	0.988	2.792	155
loamy sand	1.1	0.98	9.221	0.988	9.111	1427

loam	4.5	0.99	11.054	0.994	10.987	420
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¹ Adj. Factors derived for different 1/N values & conc. ranges based on van Genuchten et al. (1977) and Parker and Jardine (1980)

² $K_{dl} = (K_p) * (\text{Adj. Factor})$

³ $K_{oc} = (K_{dl} * 100) / \%OC = (K_{dl} * 100 * 1.724) / \%OM$

Freundlich K_{des} values were 11.2 for the sand soil, 0.71 for the clay soil, 0.23 for the loamy sand soil, and 0.31 for the loam soil. Respective 1/N values were 1.3, 1.0, 0.83, and 0.96.

3. Batch equilibrium data for reference chemicals of known mobility were not submitted. The study authors stated that the loamy sand soil was sterilized using chloroform fumigation to decrease the influence of microbial activity (p. 15). This procedure could affect the adsorption of the pesticide by the soil. In the future registrant-conducted studies, if sterilized soils are used to study test compound mobility, additional batch equilibrium studies must be conducted using reference chemicals of known mobility.
4. The study authors stated that the loamy sand soil (from North Carolina) utilized in this study was the same type of soil used in an aerobic soil metabolism study (p. 11; MRID 44457785). We note that a sandy loam soil from Holy Springs, North Carolina, was utilized in the aerobic soil metabolism study.
5. Method detection limits (MDL) and limits of quantitation (LOQ) were not reported for either LSC or HPLC analyses of the prohexadione calcium.

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PROHexadione Calcium

DER MRID 44457787

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Pages 6 through 17 are not included.

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- ☐ Description of quality control procedures.
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